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Dielectric behaviour of solution grown poly(vinyl) pyrrolidone films

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Abstract : Measurements on dielectric relaxation in poly(vinyl) pyrrolidone (PVP) films, of approximately 20 microns in thickness, were made for similar (Al-Al) and dissimilar (Al-Sn/Cu/Ag) electrode combinations in the frequency range (500 Hz–20 kHz) and temperature range (40–200°C). PVP films exhibit two dielectric loss maxima, one around 100 ± 5°C and the other around 170 ± 5°C, respectively With increasing frequency, the magnitudes of capacity and of both the loss peaks decrease and also the loss peak positions shift towards higher temperature side Pronounced effect of electrode material on the capacity and loss peaks has also been observed. The results of the experiments and the mechanisms involved have been discussed.

Keywords : Poly(vinyl) pyrrolidone, capacity and losses; dipole-dipole interactions

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Dielectric studies are of special interest in relation to polymers since they provide vital information on the molecular configuration of a system. The evaluation of the dielectric properties of insulator films is carried out by measuring simultaneously the capacitance and dissipation factor over a wide range of frequencies and temperatures. A knowledge of the dielectric loss behaviour of thin polymer films is very important because of their possible technical application for insulation, isolation and passivation in microelectronic circuits. The capacity and the dissipation factor are the crucial quantities required in the design of devices and furthermore, as a function of temperature or frequency they reveal much information on the chemical or physical state of the polymer.

Dielectric behaviour of a number of polar and nonpolar polymers have been investigated in the last decade [1–5]. Poly(vinyl) pyrrolidone (PVP) is known to be of a growing pharmaceutical importance [5–7]. A systematic study of dielectric behaviour over

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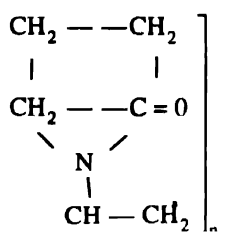
a range of frequencies and temperatures was undertaken to understand the nature of the relaxations in PVP.

Poly(vinyl) pyrrolidone (PVP), molecular weight 40,000 was obtained from M/s Loba Chemical, Bombay. PVP is known as a polar polymer, due to its carbonyl group of double bond in pyrrolidone ring [8]. The network structure of PVP has different length of π and σ bonds in between, nitrogen, oxygen, carbon and hydrogen atoms [9,10]. The asymmetric distribution of electronic charges near different atoms (N, O, C and H) may be possible in PVP, hence it is known as a disordered material. In PVP, the asymmetric monomers are present in the structure and it possesses a side group (as pyrrolidone ring). Its structure is as follows [11].



The solution was prepared in a glass beaker by dissolving 2.1 g PVP in 30 cm^3 of chloroform at room temperature. The solution was continuously stirred for about 30 min by means of a teflon-coated magnetic stirrer. Thereafter, the solution was stirred and heated to 50°C to ensure a homogeneous mixing of the solvent. The glass beaker containing the solution was then immersed in a constant temperature oil bath. Ultrasonically cleaned glass slide were immersed vertically into the solution for a period of 30 min. After the film deposition, the glass slide was taken out and outgassed in air at 50°C for 24 hrs. followed by room temperature outgassing at 10^{-5} torr for a further period of 24 hrs. Vacuum coated electrodes were used throughout the work. The thickness of the sample was approximately 20 microns. The geometry of the sandwich configuration of the electrodes, and thickness of the sample was same as reported earlier [12,13].

The assembly was held in a thermostat and the temperature was measured using calibrated copper-constantan thermocouple. The capacitance and losses were measured with a Systronics LCR bridge Type 921 using a Philips AF generator model GM 2308/90.

Figure 1 shows the capacity of PVP films as a function of temperature at different frequencies (500 Hz, 1 kHz, 5 kHz, 10 kHz and 20 kHz). The capacity values have been found to decrease with increasing frequency. Figure 2 shows the capacity value of PVP as a function of frequency (log f) at constant temperatures. Figure 3 shows the losses at different frequencies as a function of temperature for similar electrode (Al–PVP–Al) system. The loss curves have been found with two maxima aroud 100 ± 5°C and 170 ± 5°C, respectively. Figure 4 shows the variation of loss of PVP films with similar (Al–Al) and

dissimilar (Al–Sn/Cu/Ag) electrode systems. Both the loss peaks shift towards higher temperature. It is observed that the magnitude of capacity and loss peaks are higher in the case of the dissimilar electrode system than in the case of Al–Al electrode system.

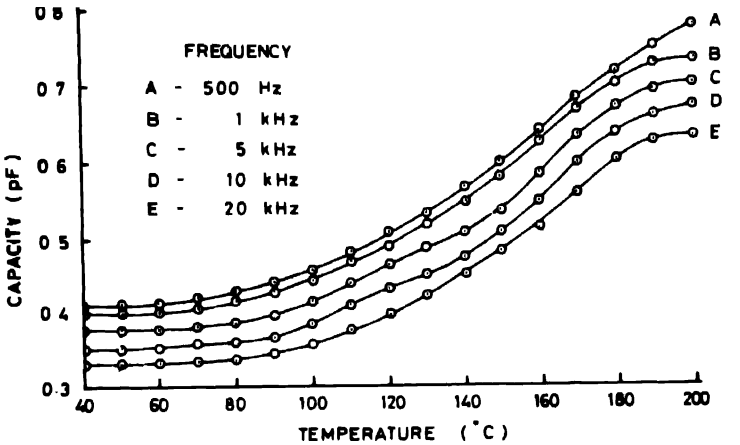


Figure 1. Variation of capacity with temperature at different frequencies for Al–PVP–Al samples

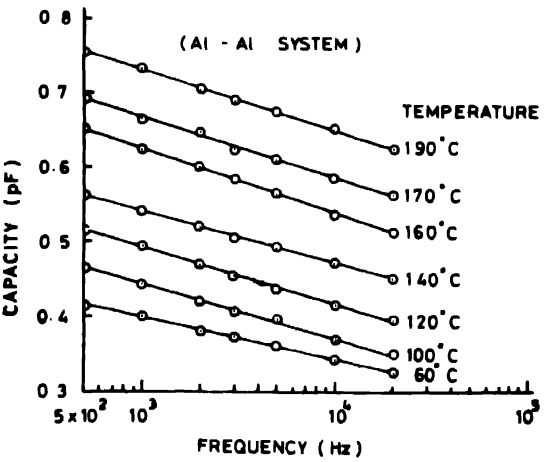


Figure 2. Capacity *versus* log *f* for Al–PVP–Al samples at different temperatures.

The carbonyl group of PVP may possess orientation with respect to the active groups [14]. The different types of rotational motions of polar groups of PVP structure attribute to higher losses. The maximum value of losses (loss peak) in certain temperature regions are possible, due to phase transition behaviour of PVP. At a certain temperature, the side chains are immobile. These chains are tightly bound at different points due to dipole-dipole interactions of pyrrolidone groups. As the temperature is increased, more and more polar groups are released from their bound state. The higher dipole moment of pyrrolidone

adjacent group and their strong dipole interactions with the main chain might be responsible for the higher dielectric losses in PVP.

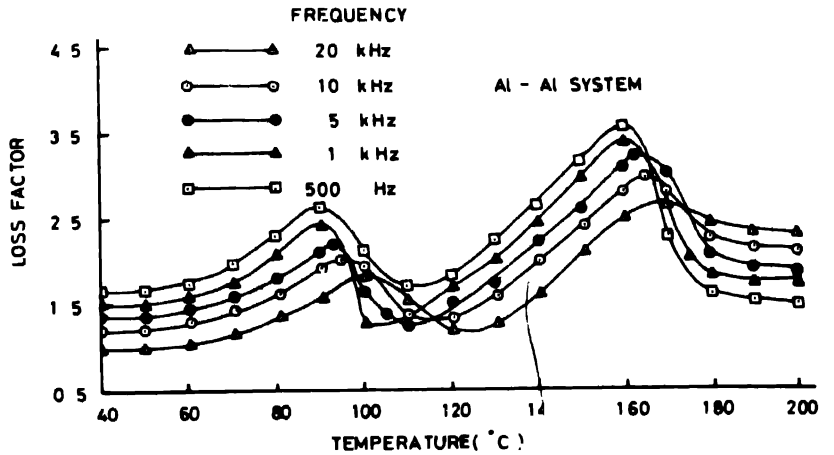


Figure 3. Variation of loss factor with temperature at different frequencies for Al–PVP–Al samples.

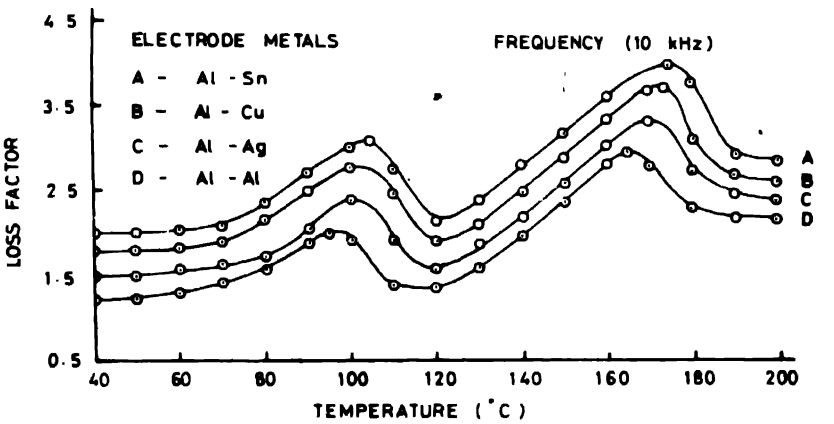


Figure 4. Variation of loss factor with temperature at constant frequency for dissimilar electrode (Al–PVP–Sn, Al–PVP–Cu and Al–PVP–Ag) combinations.

The increase in capacity values above the room temperature may be due to increase in molecular mobility and also may be partly due to the expansion of the lattice [15] and partly due to the excitation of charge carriers which are likely to be present inside the specimen at the imperfection sites. At lower temperature, molecules are immobile and therefore, the number of dipoles which facilitate to orient with the field will be less. Increase in temperature increases the molecular mobility and therefore, more number of dipoles orient themselves in the field direction. The amorphous-crystalline interphases in PVP behave as trapping centre for carriers [5]. Since the arrangement of molecules in the

amorphous state is not regular, the van der Wall's forces between the molecules vary from place to place. It is therefore, easy to conform or move the molecular chains in the amorphous state. The molecular packing in the amorphous regions is loose and so the density is smaller than that of crystalline regions. Thus, the chains in the amorphous phase are more flexible and are capable of orienting themselves, relatively more easily and rapidly. In crystalline regions, the forces which hold the structural units together are of a homopolar chemical binding nature and are much stronger than the van der Wall's forces. Therefore, the movement of a segment of chains in the higher density crystalline regions is hindered by other neighbouring structural units. The molecular chains with different mobilities for the amorphous-crystalline regions try to adjust themselves in such a way as to add to the polarization of the system [16]. This molecular alignment of chains may cause the observed increase in the capacity values.

The variation in capacity and loss values, suggests the net effect of some internal field within the polymer alongwith the external *ac* field. The dipole-dipole interactions between the different groups or many body interactions suggest the lower losses with higher frequency range. The dependence of the capacity on frequency can be determined from the following equation [17]

$$C = C_g + \frac{S\tau}{1 + \tau^2 W^2} \tag{1}$$

where C_g is the geometrical capacitance, S the conductance corresponding to the absorption current, τ the dipole relaxation time and W the angular frequency. The above equation show that C should diminish with increasing frequency.

The increase in losses (Figure 3) at low frequency could be associated with the polarization of the trapped charge carriers. With the increase in frequency, polarization decreases and becomes vanishingly small at high frequencies. The decrease in losses with frequency also seems to show the decrease in the number of charges and delay in settling of dipoles due to availability of very short time in one half cycle of alternating voltage. The general expression for dielectric loss is given by the equation [17]

$$\tan\delta = \frac{W^2\tau^2(G_{in} + S) + G_{in}}{W\left\{S\tau + C_g(W^2\tau^2 + 1)\right\}}, \tag{2}$$

where G_{in} is the conductance for the residual current. From eq. (2)

$$\lim_{W \to 0} \quad \tan\delta = \infty,$$

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Differentiating eq. (2) with respect to W and then equating the derivative to zero, it is possible to obtain the value of W' of the frequency corresponding to maximum loss.

The loss peak at 170 ± 5°C may be attributed to segmental mobility of glass transition type and also to release of all types of ions/carriers at glass transition range (T_g) of PVP (around 170°C). The side group (C=O) is attached with nitrogen atom of PVP. This group is combined with other active groups (>N–C=O), hence there may be a larger number of dipoles apart from the molecular motion and a higher amount of energy must be associated with the rotation of adjacent side of the polymer structure. The rotational energy alongwith many body interaction at or near T_g (second loss peak) must be associated with different atoms of main chain such as C–C or C–N atoms. These bonds of nitrogen and oxygen are different in nature and they posses different types of binding tendencies between C, O and N atoms. At T_g of the polymer, the bonds are loosened to some extent and results a higher loss peak in higher temperature range, whereas, the local motion of adjacent group is associated in comparatively lower region of temperature. PVP forms a complex network of conjugated chemical reactions in the presence of moisture. The chemical reactions in complete phase transition may be given by

$$H\,O\,H \rightleftharpoons H^+ + OH^-$$

$$>N\underset{|}{-C}=O + OH \rightarrow N\text{–}COOH + H^+ + e^-.$$

The dissociated water may produced the H^+ and OH^- pair. The ionic/electronic charge carriers released at rubber glass transition temperature and the complete phase transition is observed with a sterio-change in its long chain structure. The loss peak has been found at 100 ± 5°C is related to the unfreezing of side group motion in less ordered domain and the second loss peak (at about 170 ± 5°C) is associated to the unfreezing of segmental mobility within the non-crystalline clusters and possibly to the appearance of a certain mobility of different results of loss peaks can be understood with the help of different considerations of the PVP structure.

Figure 4 exhibits the variation of losses *versus* temperature for electrode metals, aluminium, copper, silver and tin having work function 3.38, 4.46, 4.31 and 4.09 eV, respectively. It is clear from the figures that the losses (at different temperatures) differ when the upper electrode aluminium is replaced by copper, silver or tin. The magnitude of loss peaks were found to be higher in dissimilar electrode (Al–Cu and Al–Ag) than similar electrode (Al–Al) combinations. This shows the effect of the materials of electrodes on losses of the sample sandwiched between them. Values of losses seem to be controlled by the effective work function of metal-insulator-metal interfaces *i.e.* the difference in energy between the Fermi level in metal and the bottom of the conduction band in the insulator. Therefore, dielectric parameters are changed when the electrode forming material is changed. The difference between the work function of metal (1) and metal (2) will control the magnitude of loss but for Al–Al electrode system, the characteristics of the polymer may prevail as the net contribution of charges injected from the electrodes would then be zero [18,19]. The various thermograms represent the distributed relaxations in terms of loss peaks. The reason for distributed relaxations may be due to the combined effect of space charge injected from electrodes and dipolar relaxations in the polymer. The appearance of

the peaks at distributed position is perhaps due to uniform polarization. In these results, it is also suggestive that the internal field of polymer may get modified by the difference in the work function of various electrode metals [20].

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